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Dichloro[(6*R*,7*S*,8*S*,14*S*)-(−)-sparteine-κ^2N,N']mercury(II)

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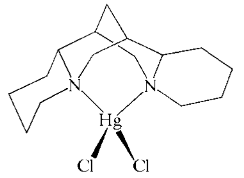
In the title compound, $[\mathrm{HgCl_2(C_{15}H_{26}N_2)}]$, the chiral alkaloid (6*R*,7*S*,8*S*,14*S*)-(−)-L-sparteine acts as a bidentate ligand, with two $\mathrm{Cl^-}$ ligands occupying the remaining coordination sites, producing a distorted tetrahedron. The N—Hg—N plane is twisted by 81.1 (2)° from the Cl—Hg—Cl plane. The mid-point of the N···N line does not lie exactly on the Cl—Hg—Cl plane but is tilted towards one of the N atoms by 0.346 Å. Similarly, the mid-point of the Cl···Cl line is tilted toward one of the Cl atoms by 0.163 Å. The packing structure shows that the complex is stabilized by two interatomic Cl···H contacts involving both Cl atoms and the methylene or methine H atoms of the (−)-sparteine ligand.

Comment

(−)-Sparteine (spar), a naturally occurring tertiary diamine, has been intensively utilized in medicinal chemistry (Cady *et al.*, 1977), in the asymmetric synthesis of chiral compounds (Beak *et al.*, 1996; Kretchmer, 1972; Mason & Peacock, 1973) and in the preparation of a model compound for the type I copper(II) site in metalloproteins (Kim *et al.*, 2001). The structures of several metal(II) sparteine dichloride complexes of the type $[MX_2(\mathrm{spar})]$ ($M = \mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$ or $\mathrm{Zn^{II}}$, and $X = \mathrm{Cl^-}$ or $\mathrm{Br^-}$) have been reported, and the metal moieties in these compounds are known to have a distorted tetrahedral geometry (Kang, Choi *et al.*, 2004; Kang, Lee *et al.* 2004; Kuroda & Mason, 1979; Lee *et al.*, 2002, 2003; Lopez *et al.*, 1998; Lorber *et al.*, 2002).

The zinc(II) ion has a closed-shell d^{10} electronic structure, and consequently the molecular structure of $[\mathrm{ZnCl_2(spar)}]$ (Lee *et al.*, 2003) is thought to be determined solely by the steric effect of the (−)-sparteine ligand operating on the $\mathrm{ZnCl_2}$ unit. The two Zn—N bond distances in $[\mathrm{ZnCl_2(spar)}]$ [2.085 (7) and 2.087 (7) Å] are nearly equal and the dihedral angle between the N1—Zn—N9 and Cl1—Zn—Cl2 planes is 82.2 (2)°, only 7.8° smaller than the value of 90° for a perfect tetrahedron. Although the two Cu—N bond distances [2.003 (13) and 2.021 (11) Å] in $[\mathrm{CuCl_2(spar)}]$ (Lopez *et al.*, 1998) are equal within two standard deviations, a smaller dihedral angle of 67.0° was observed between N1—Cu—N9 and Cl1—Cu—Cl2. This is definitely the result of the balance of the electronic effect of the d^9 system and the steric effect imposed by the bulky (−)-sparteine ligand. The electronic effect of the d^9 configuration on the geometry of four-coordinate $\mathrm{Cu^{II}}$ complexes tends to prefer a square-planar to a tetrahedral structure (Figgis, 1966).



(I)

The synthesis of the title compound, (I), was prompted by our interest in the preparation of a momomeric and tetrahedral $\mathrm{Hg^{II}}$ compound and a desire to compare the coordination geometry and bonding parameters of (I) with the analogous $\mathrm{Cu^{II}}$ and $\mathrm{Zn^{II}}$ sparteine dichloride complexes for which structures are already known (Lee *et al.*, 2003; Lopez *et al.*, 1998).

The crystal structure of (I) was determined and selected bond distances and angles for (I) are listed in Table 1. The complex is monomeric and shows the expected overall geometric features, with the (−)-sparteine molecule acting as a bidentate ligand in an all-chair conformation. The coordination around the $\mathrm{Hg^{II}}$ atom is best described by a slightly distorted tetrahedron. The mid-point of the N1···N9 line of the sparteine ligand does not lie in the Cl1—Hg—Cl2 plane, but is tilted towards atom N1 by 0.346 Å (23.1% of half the N1···N9 distance). Similarly, the mid-point of the Cl1···Cl2 line is tilted toward atom Cl2 by 0.163 Å (7.6% of half the Cl1···Cl2 distance). The N1—Hg—Cl1 bite angle is 4.35° smaller than the N9—Hg—Cl2 bite angle. However, the N1—Hg—Cl2 bite angle is 5.6° larger than the N9—Hg—Cl1 bite angle.

The dihedral angle between the N1—Hg—N9 and Cl1—Hg—Cl2 planes in (I) is 81.1 (2)°, which is quite similar to that

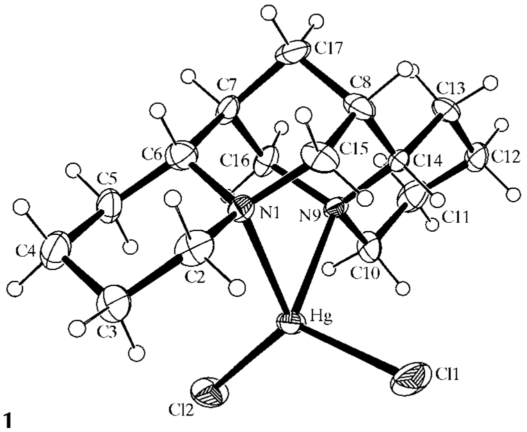


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

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between the N1—Zn—N9 and Cl1—Zn—Cl2 planes in [$ZnCl_2$(spar)]. However, the two Hg—N and the two Hg—Cl bond distances in (I) differ significantly (Table 1), whereas the two Zn—N and the two Zn—Cl bond distances in [$ZnCl_2$(spar)] are nearly identical, respectively (Lee *et al.*, 2003). Asymmetry in the two M^{II}—N bond distances was also observed in [$CoCl_2$(spar)] [2.040 (7) and 2.068 (8) Å; Kuroda & Mason, 1979], and was considered to be attributed to the *cis*- and *trans*-ring junctions of the rings including atoms N1 and N9, respectively (Lorber *et al.*, 2002). However, the observation of the asymmetry in the two Hg^{II}—N bond distances in the d^{10} compound, (I), is somewhat surprising, since the two M^{II}—N bond distances in another d^{10} complex, [$ZnCl_2$(spar)], and in a high-spin d^5 complex, [$FeCl_2$(spar)] (Lee *et al.*, 2003; Lorber *et al.*, 2002), in which the electronic effect on the coordination geometry is not operative, are almost identical.

The crystal structure of (I) is stabilized through two interatomic Cl···H contacts involving two Cl atoms and the methylene or methine H atoms of the (−)-sparteine ligand, namely Hg—Cl1···H15B^{i} and Hg—Cl2···H7^{ii} (Table 2). The Cl···H separations are then 0.22 and 0.17 Å shorter, respectively, than the sum of the Cl and H van der Waals radii (Pauling, 1960).

The asymmetry in the two Hg—N bond distances in (I) might be attributable either to the poorer Lewis acidity of Hg^{II} or to the intermolecular Cl···H interaction in the crystalline packing structure.

Experimental

The title complex was prepared by the direct reaction of mercury(II) chloride with a stoichiometric amount of (−)-L-sparteine in an ethanol–triethyl orthoformate (5:1 *v*/*v*) solution. The resulting colourless precipitate was filtered off, washed with cold absolute ethanol and dried in a vacuum. Single crystals of (I) were obtained by recrystallization at room temperature from a dichloromethane–triethylorthoformate (5:1 *v*/*v*) solution. Analysis calculated for $C_{15}H_{26}Cl_2HgN_2$: C 35.61, H 5.18, N 5.54%; found C 35.69, H 5.23, N 5.65%.

Crystal data

[$HgCl_2(C_{15}H_{26}N_2)$]
M_r = 505.87
Orthorhombic, $P2_12_12_1$
a = 11.191 (3) Å
b = 12.1156 (11) Å
c = 12.6742 (10) Å
V = 1718.4 (5) Å^3
Z = 4
D_x = 1.955 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 11.5–12.7°
μ = 9.26 mm^{-1}
T = 293 (2) K
Block, colourless
0.26 × 0.23 × 0.2 mm

Table 1
Selected geometric parameters (Å, °).

Hg—N1	2.353 (7)	Hg—Cl1	2.397 (3)
Hg—N9	2.391 (6)	Hg—Cl2	2.374 (2)
N1—Hg—N9	78.2 (3)	N9—Hg—Cl1	108.3 (2)
N1—Hg—Cl1	101.55 (18)	N9—Hg—Cl2	105.8 (2)
N1—Hg—Cl2	123.90 (19)	Cl1—Hg—Cl2	127.48 (11)

Table 2
Interatomic Cl···H contact distances (Å) and Hg—Cl···H contact angles (°) in the crystal packing of (I).

	Cl···H	Hg—Cl···H
Hg—Cl1···H15B^{i}	2.78	145
Hg—Cl2···H7^{ii}	2.83	157

Symmetry codes: (i) $\frac{3}{2}-x, -y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$.

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.099, T_{max} = 0.154
5070 measured reflections
3935 independent reflections
3052 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.5°
h = −14 → 14
k = −1 → 15
l = −1 → 16
3 standard reflections every 400 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.082
S = 1.01
3935 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}
Absolute structure: Flack (1983), with 1694 Friedel pairs
Flack parameter: −0.001 (14)

The H atoms of the sparteine ligand were positioned geometrically and constrained to ride on their attached atoms, with C—H distances in the range 0.97–0.98 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1265). Services for accessing these data are described at the back of the journal.

References

Beak, P., Basu, A., Gallagher, D. J., Park, Y. S. & Thayumanavan, S. (1996). *Acc. Chem. Res.* **29**, 552–560.

Cady, W. A., Boschmann, E., Choi, R. S., Heidelman, J. F. & Smith, S. L. (1977). *Inorg. Chem.* **16**, 1958–1961.

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Figgis, B. N. (1966). *Introduction to Ligand Fields*. New York: John Wiley & Sons Inc.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.

Kang, S. K., Choi, S.-N. & Lee, Y.-M. (2004). *Acta Cryst.* C**60**, m174–m176.

Kang, S. K., Lee, Y.-M., Kim, Y.-I., Kim, Y., Seff, K. & Choi, S.-N. (2004). *Inorg. Chim. Acta*, **357**, 2602–2608.

Kim, Y.-J., Kim, S.-O., Kim, Y.-I. & Choi, S.-N. (2001). *Inorg. Chem.* **40**, 4481–4484.

Kretchmer, R. A. (1972). *J. Org. Chem.* **37**, 2744–2747.

Kuroda, R. & Mason, S. F. (1979). *J. Chem. Soc. Dalton Trans.* pp. 727–730.

Lee, Y.-M., Kang, S. K., Kim, Y.-I. & Choi, S.-N. (2002). *Acta Cryst.* C**58**, m453–m454.

Lee, Y.-M., Kwon, M.-A., Kang, S. K., Jeong, J. H. & Choi, S.-N. (2003). *Inorg. Chem. Commun.* **6**, 197–201.

Lopez, S., Muravyov, I., Pulley, S. R. & Keller, S. W. (1998). *Acta Cryst.* C**54**, 355–357.

Lorber, C., Choukroun, R., Costes, J.-P. & Donnadieu, B. (2002). *C. R. Chim.* **5**, 251–255.

Mason, S. F. & Peacock, R. D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 226–228.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell University Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.